BASIC RESEARCH YIELDS MAJOR BREAKTHROUGH IN APPLICATION OF DIAMOND-LIKE COATINGS

SANDIA DISCOVERS PROCESS TO RELIEVE COMPRESSIVE STRESS IN CARBON FILMS DURING PARTNERSHIP WITH MOTOROLA

Researchers at Sandia National Laboratories have developed a process to create stress-free amorphous (non-crystalline) diamond films. The new material enables the creation of ultra-hard wear-resistant coatings and can also be used to create very thin free-standing membranes. Sandia made the discovery in the course of a Motorola-Sandia partnership that was researching the use of carbon-based materials for flat-panel displays. Ultra-thin carbon membranes are of value for high sensitivity micro-sensors, such as those used in monitoring the aging of the weapons stockpile, for ultra-reliable MEMS (micro-electro-mechanical systems) for surety applications, and as windows for light, x-ray, or electron optics.

Stress-free amorphous diamond material can now be created as thick ultra-hard coatings or as free-standing membranes as shown above. These membranes are one inch in diameter and only 0.1 µm thick (about 500 atomic layers). The slightly rotated membrane on the left reflects light, demonstrating that the very clear window is actually there, while the membrane on the right reveals the membrane's transparency. Ultra-thin diamond membranes are of value for high sensitivity micro-sensors, such as those used in monitoring the aging of the weapons stockpile, and as windows for light, x-ray, or electron optics.

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Sometimes it's better *not* to know what you're looking for. Ask Sandia National Laboratories' scientist John Sullivan who, with colleague Tom Friedmann, originated a stress-relaxation technique (see sidebar) for amorphous (non-crystalline) diamond films that represents a major breakthrough in hard carbon films. The discovery, which has

> **"We now have more understanding of the properties of amorphous diamond. . . . The fact that Motorola asked us to look at the fundamentals of these materials has opened a lot of doors."** *Ellen Stechel—Sandia*

significant ramifications for DOE's Defense Programs, was made during the course of basic research on the structural and electrical properties of amorphous carbon as part of a collaborative effort with scientists at Motorola's Corporate Research Labs—now part of Motorola's Flat-Panel Display Division (see box on back of this page).

Sandia and Motorola began collaborating in 1992 to gain an understanding of carbon's unique properties. Motorola's interest was in carbon's field-emission properties, which it was hoped, would revolutionize flat-panel display technology. Motorola scientists chose to partner with Sandia because they were enthused about Sandia's programs in diamond and carbon films, particularly Mike Siegal's research on diamond-like films for electronics. As part of the comprehensive research effort, Friedman and Sullivan investigated the stress evolution of amorphous diamond films.

Serendipitous Discovery

"It wasn't our intent to discover a stress-free amorphous diamond material," Sullivan said. "We were performing basic materials research on the properties of carbon films, and stress is one way to characterize a material."

Ordinarily, amorphous diamond films have very high levels of compressive stress, which causes the film to peel off its substrate—like a thick layer of weathered paint—making it impossible to create thick coatings or large area free-standing membranes. But Sandia scientists learned that heating amorphous diamond films eliminated film stress, while allowing the material to retain its diamond-like properties, such as hardness, high wear resistance, low coefficient of friction, and resistance to most chemicals.

"These hard amorphous carbon films have most of the desirable properties of crystalline diamond with none of the processing drawbacks," said Ellen Stechel, manager of the Advanced Materials and Device Sciences department at the time. "Initially, we were trying to understand the electrical properties, anticipating that fundamental insight in the anomalous electrical behavior would be essential for understanding emission phenomena. But in the process of doing good science, we learned a lot more. And John and Tom were clever enough to see that a stress-free material opens up the possibilities for a number of exciting applications."

Harder Than Any Known Coating

The Sandia stress-free amorphous diamond films are harder than any known coating, except for crystalline diamond, with 95% of diamond's hardness and stiffness. Friedmann and Sullivan have demonstrated the ability to place these ultra-hard coatings on nearly any substrate, including soft plastic.

Sandia's patent-pending stress-relieving process also makes it possible to tailor the film stress, which means that researchers can grow a large area, stress-free, slightly compressive or even slightly tensile, amorphous diamond free-standing membrane. These membranes are of

Stress Relaxation 101

The ability to create a stress-free amorphous diamond film relies on a process known as stress relaxation. "The stress relaxation that occurs in these amorphous diamond films is uniquely different from other types of stress relaxation we have seen in the past," said John Sullivan of Sandia, who co-discovered the process with colleague Tom Friedman.

The stress relaxation that occurs in amorphous diamond involves an internal bond rearrangement process. As Sullivan describes it, "Imagine compressing a carton of volleyballs. Now imagine that some of those volleyballs can permanently transform into footballs. If enough volleyballs are transformed, then the whole carton of balls adjusts to the force being applied to it. Something similar happens when amorphous diamond stress relieves—except it happens at the atomic level."

Surprisingly, the hardness and other characteristics of the material are unaffected by such rearrangements at the atomic level.

value for ultra-sensitive micro-sensors and windows for light, x-ray, or electron optics.

Defense Programs Benefit

Some defense programs applications for which the stress-free coating is well-suited include micro-sensors for monitoring the nuclear weapons stockpile, and ultra-reliable MEMS (micro-electro-mechanical systems) for surety applications.

To ensure the reliability of the stockpile in the absence of testing and new weapon development, high performance and rugged micro-sensors are needed to monitor the environment around the weapon and the aging of the components within the weapon. Reliable MEMS are proposed to replace some of the larger surety components within the weapon, thus simplifying their operation and reducing the total number of parts needed for the component.

Offers Major Advantages

"Currently, most membrane-based sensors are made with silicon nitride, but we think that amorphous diamond will offer major advantages," said Sullivan. "We are partnering with Sandia's Microsensor Research and Development Department to develop a magnetically-excited flexural plate wave sensor that will use an ultra-thin amorphous diamond membrane. With stress-free amorphous diamond, we think we can get a 50-fold improvement in sensitivity."

Because of the material's remarkable wear resistance, another tantalizing possibility is the creation of all-carbon MEMS, which are moving components on a microscale, made with conventional microelectronics photolithography. To the Defense Programs, miniaturization through the use of MEMS is particularly attractive because functionality, such as added safeguards, can be increased in a weapon.

The current MEMS program has already demonstrated how successful this concept can be. The outstanding wear resistance of stress-free amorphous diamond would enhance the possibilities by the creation of MEMS with extended lifetimes and extreme reliability.

Huge Potential

The many desirable qualities of stress-free amorphous diamond present a huge potential for future applications. And continued research into both three- and four-fold carbon films (see box above left) can be expected to strengthen the current knowledge base of this fascinating and flexible material.

"We now have more understanding of the properties of amorphous diamond, but we're still in the exploratory stage on other carbon materials," said Stechel. "Just the fact that Motorola asked us to look at the fundamentals of these materials has already opened a lot of doors." —*J. Chapman*

DOE Defense Programs funded portions of Sandia's work for this project.

Amorphous Carbon and Flat-Panel Displays

Scientists have known of the special class of hard amorphous carbon films, called amorphous diamond, since 1988 but discounted it for practical use because of its very high film stress.

This material is a hydrogen-free amorphous mixture of carbon deposited at room temperature consisting of a complex mixture of three- and four-fold coordinated carbon atoms.

By changing the growth parameters, the ratio of four-fold to three-fold varies, enabling manipulation of materials properties from hard to soft, from insulating to conducting, and from transparent to opaque.

As part of the partnership with Motorola, Sandia has conducted basic materials research on both three- and four-fold amorphous carbon films. The stress-free amorphous diamond film has high four-fold carbon content, which offers atomically smooth coatings, ultra-hard films, and optically transparent membranes. The three-fold carbon films are of particular interest to Motorola because of their superb cold-cathode electron field emission properties that enables a promising new flat-panel display technology.

"Due in part to the successful partnership between Sandia and Motorola,
Motorola is moving forward with the manufacturing of flat-panel field-emission displays," said Mike Siegal, Sandia's principal investigator for the partnership.

Flat-panel field-emission displays are similar in visibility, brightness, contrast, resolution, and color to most television and computer monitor screens that use cathode ray tubes.

Markets for flat-panel displays would include televisions that can hang on a wall, superior displays for laptop computers, medical monitors, and other small display applications.